Supporting Information

Chiral Supramolecular Gels with Lanthanide Ions: Correlation between Luminescence and Helical Pitch

Chaelin Kim,[†,§] Ka Young Kim,[†,§] Ji Ha Lee, [†,‡,§], Junho Ahn,[†] Kazuo Sakurai,[‡] Shim Sung Lee[†] and Jong Hwa Jung[*,†]

† Department of Chemistry and Research Institute of Natural Sciences Gyeongsang National University, Jinju, 660-701, Korea.

‡ Department of Chemistry, Kitakyushu University, Kitakyushu, 819-0395, Japan

Corresponding Author

Jong Hwa Jung* (jonghwa@gnu.ac.kr)

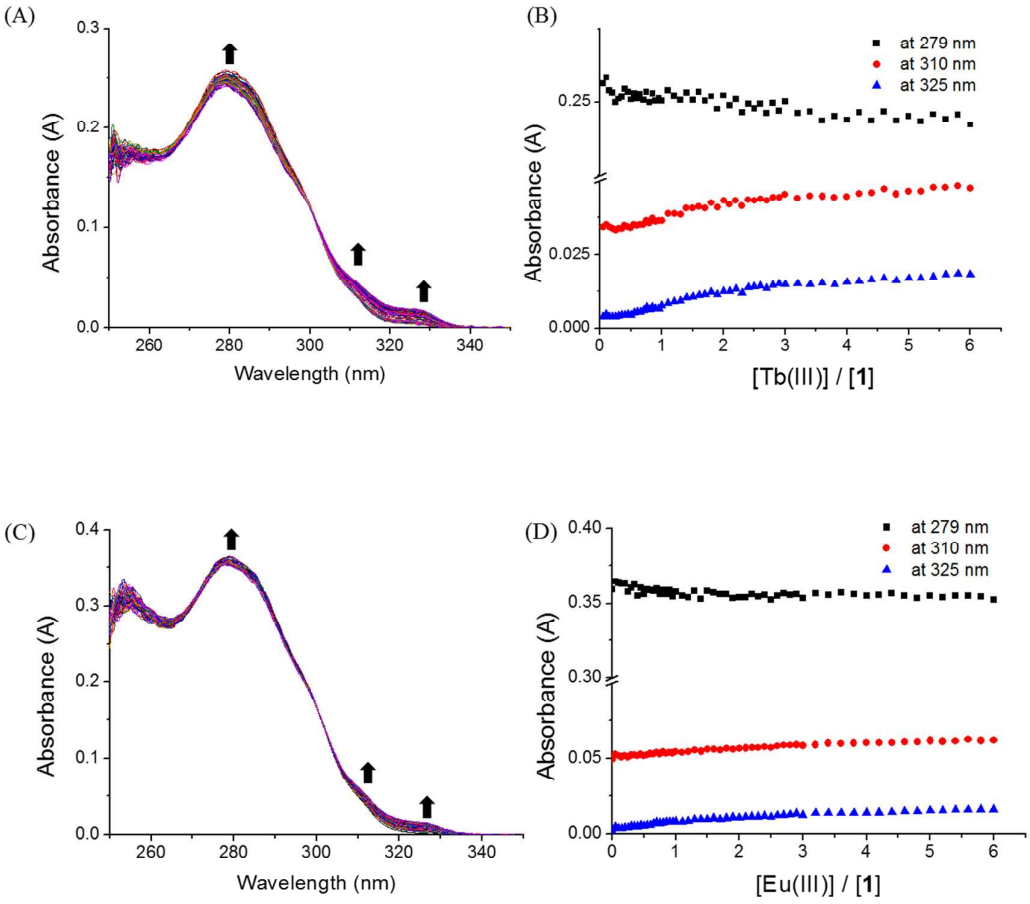

Figure S1. The absorption spectra of sol **1** (1×10^{-5} M) upon titrating with (A) $Tb(NO_3)_3$ and (C) $Eu(NO_3)_3$ (0-6.0 equiv.) in H_2O/DMSO (3:7 v/v) at 298K. Plot of absorption intensity of sol **1** (1×10^{-5} M) upon titrating with (B) $Tb(NO_3)_3$ and (D) $Eu(NO_3)_3$ (0-6.0 equiv.) in H_2O/DMSO (3:7 v/v) at 298K (cell width : 10 mm).

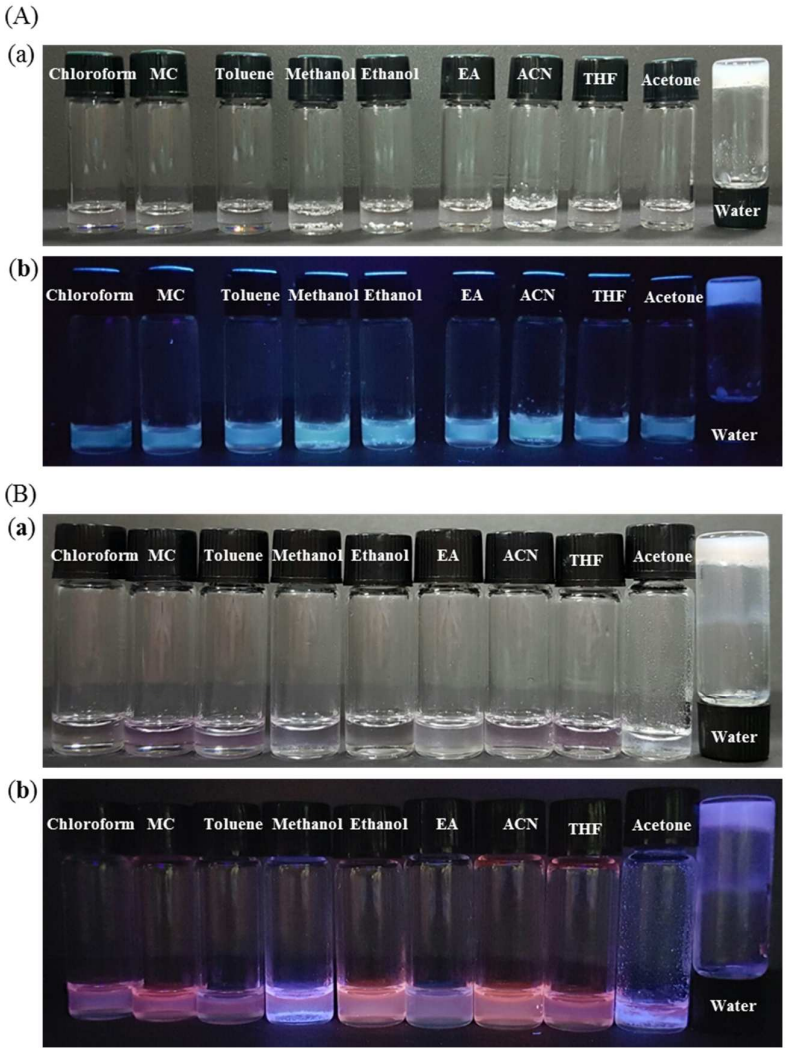

Figure S2. Photographs showing gelation test of **1** in a mixture of DMSO with (A) Tb(III) (1 equiv.) and (B) Eu(III) (1 equiv.), respectively, in various solvents taken (a) under room light and (b) under UV-lamp.

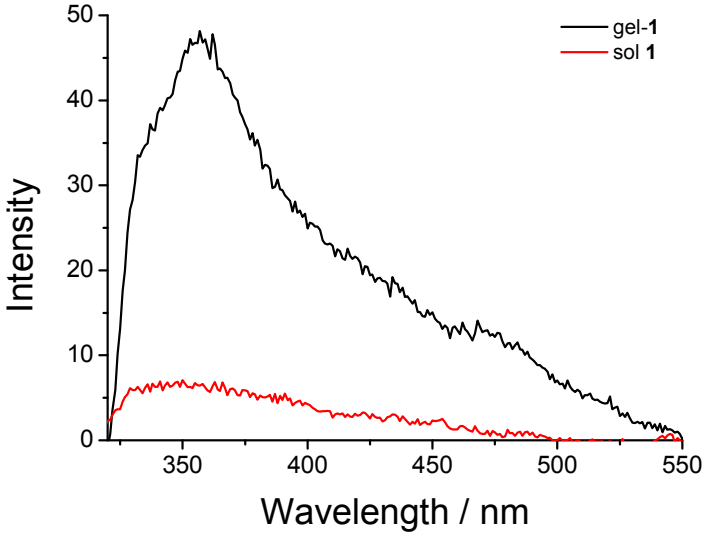

Figure S3. Fluorescence spectra of gel-**1**(black line, 1.30×10^{-3} M) and sol **1**(red line, 5×10^{-4} M).

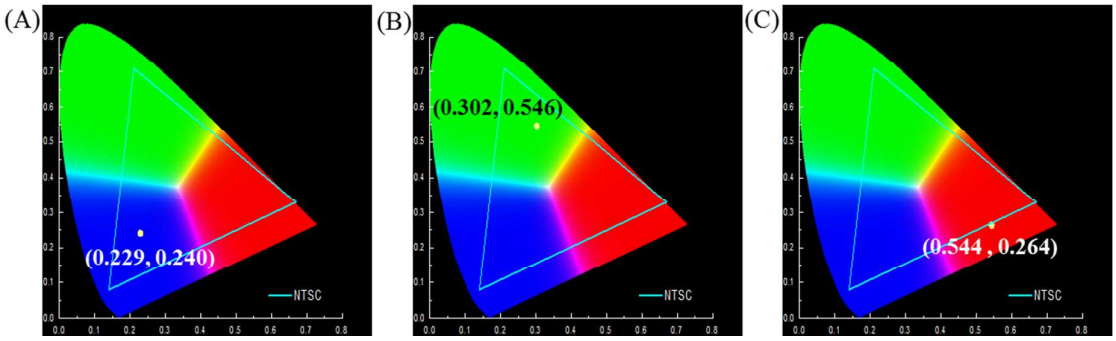

Figure S4. CIE chromaticity diagram calculated from the emission spectrum of (A) gel-**1** (1.30×10^{-3} M), (B) gel-Tb (1.30×10^{-3} M, 1 equiv.) and (C) gel-Eu (1.30×10^{-3} M, 1 equiv.).

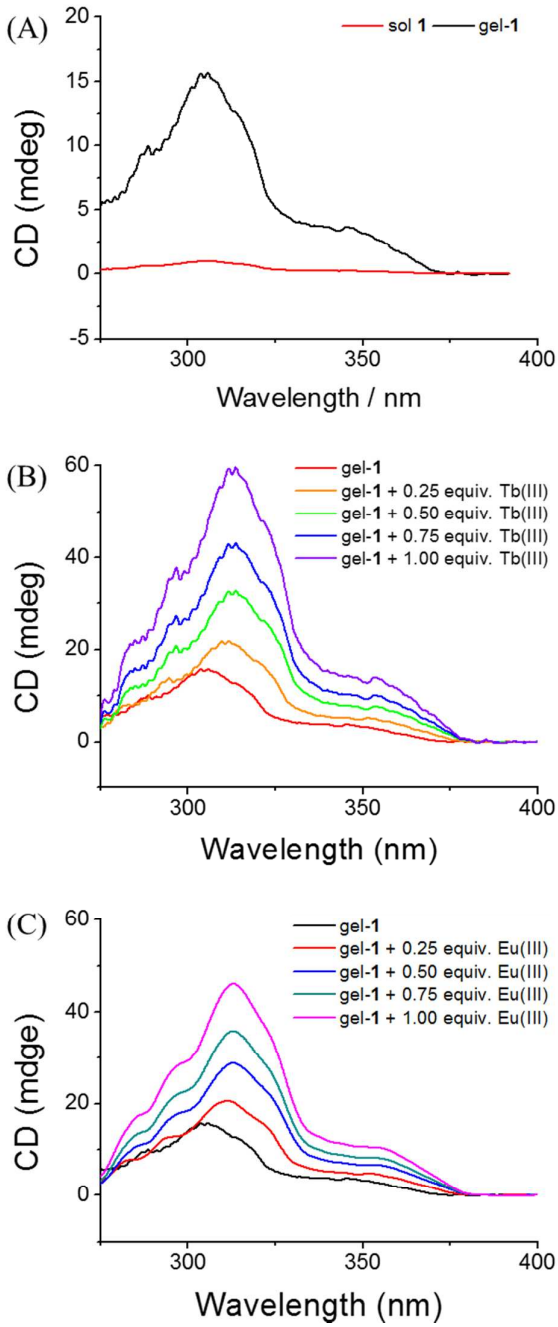

Figure S5. (A) CD spectra of gel-**1** and sol **1** (1.30×10^{-3} M). CD spectra of (B) gel-Tb and (C) gel-Eu at different metal concentration (0, 0.25, 0.5, 1.0 equiv.).

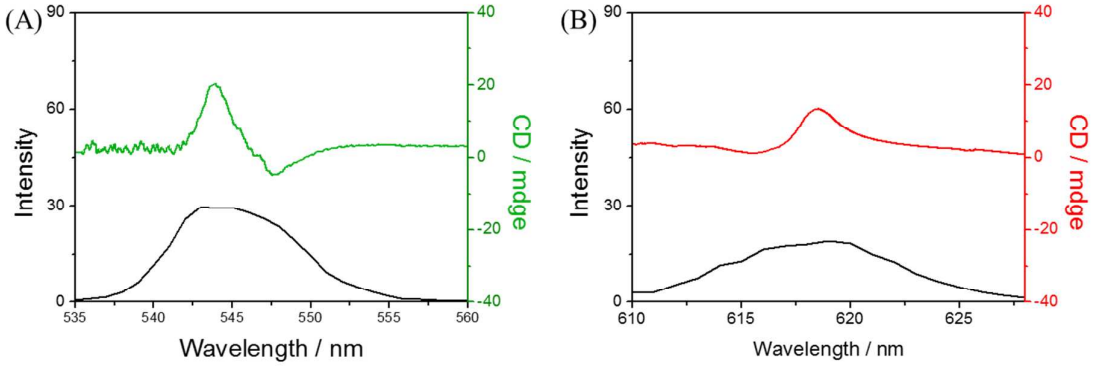

Figure S6. Luminescence (lower curves, right axis) and CPL spectra (upper curves, left axis), gel-Ln (1 equivalent) for 10^{-3} M of the (A) Ln = Eu (III) and (B) Ln = Tb(III) complexes in DMSO/H_2O (λexc = 325 nm) at 298 K.

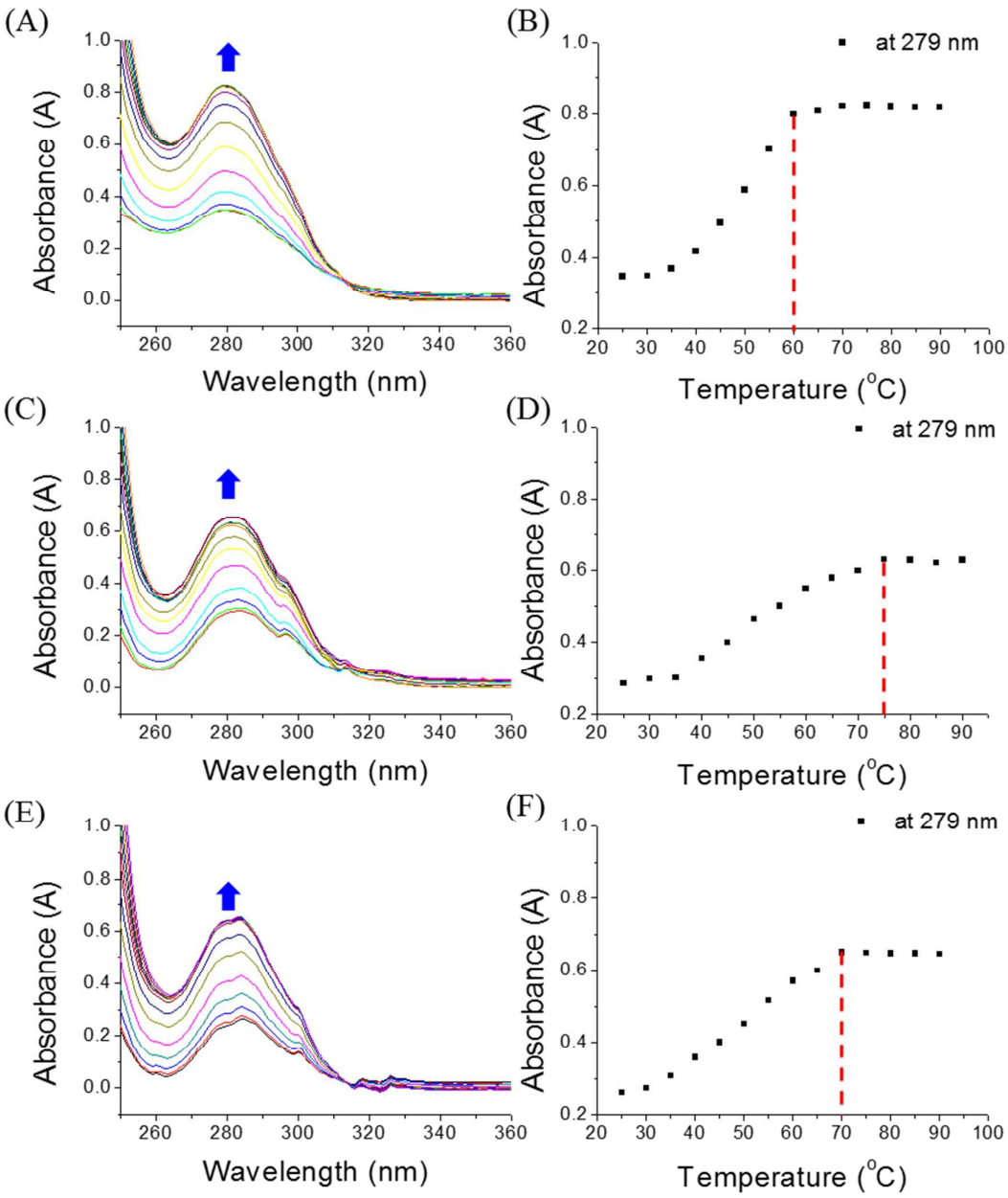

Figure S7. Absorption spectra of (A) gel-**1** (1×10^{-4} M), (C) gel-Tb (1×10^{-4}M) and (E) gel-Eu (1×10^{-4} M) at different temperatures (increasing from 298 to 363K). Plot of absorption intensity of (B) gel-**1**, (D) gel-Tb, and (F) gel-Eu absorbance against temperature (cell width : 2 mm).

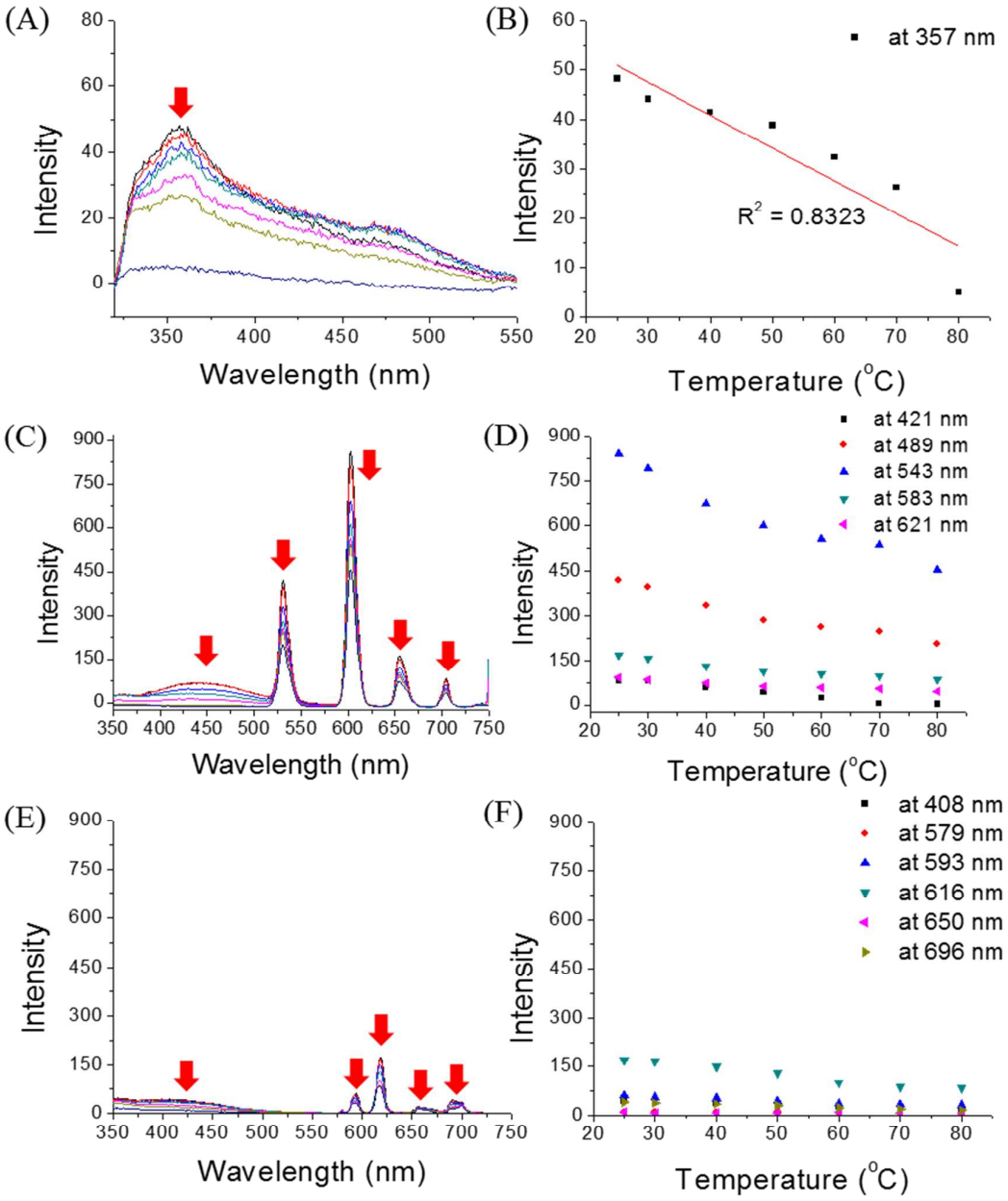

Figure S8. Luminescence spectra of (A) gel-**1** (1.30×10^{-3} M), (C) gel-Tb (1.30×10^{-3} M), and (E) gel-Eu (1.30×10^{-3} M) at different temperatures (increasing from 298 to 363K). Plot of luminescence intensity of (B) gel-**1**, (D) gel-Tb, and (F) gel-Eu luminescence against temperature (excitation : 325 nm, cell width : 2 mm).

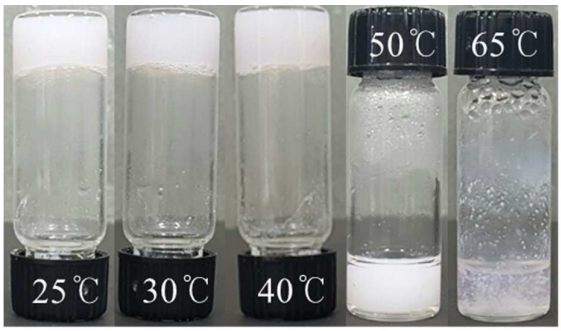

Figure S9. Photographs of gel-**1** (1 wt%) at different temperatures.

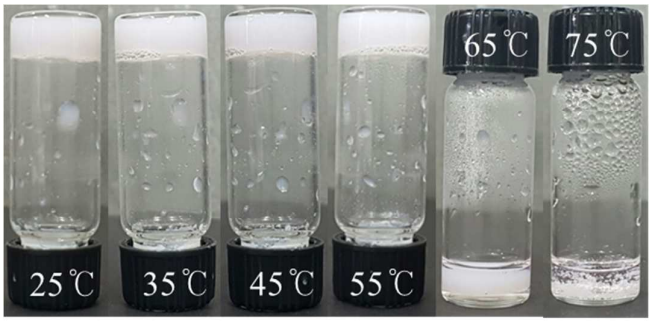

Figure S10. Photographs of gel–Tb (1 wt%) at different temperatures.
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Figure S11. Photographs of gel–Eu (1 wt%) at different temperatures.

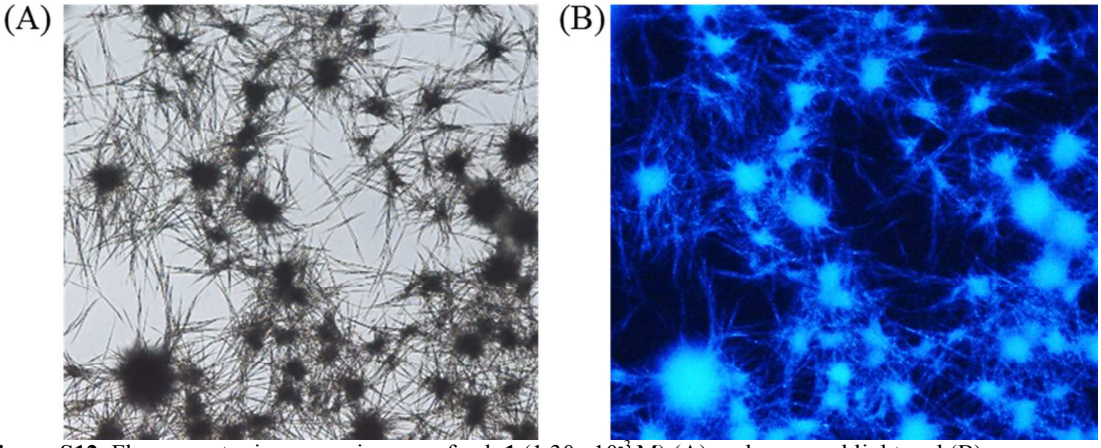

Figure S12. Fluorescent microscope images of gel–**1** (1.30×10^{-3} M) (A) under normal light and (B) fluorescence light.

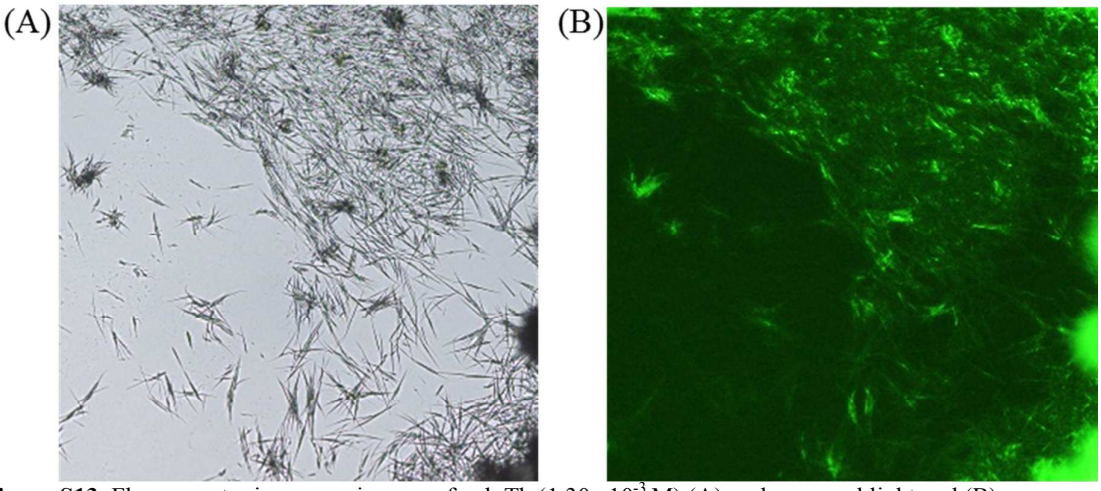

Figure S13. Fluorescent microscope images of gel–Tb (1.30×10^{-3} M) (A) under normal light and (B) fluorescence light.

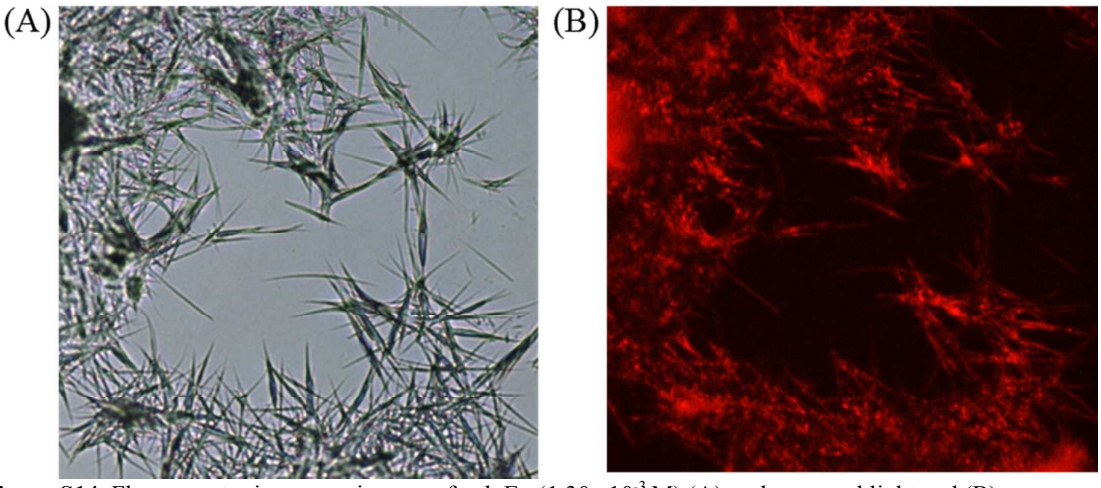

Figure S14. Fluorescent microscope images of gel–Eu (1.30×10^{-3} M) (A) under normal light and (B) fluorescence light.

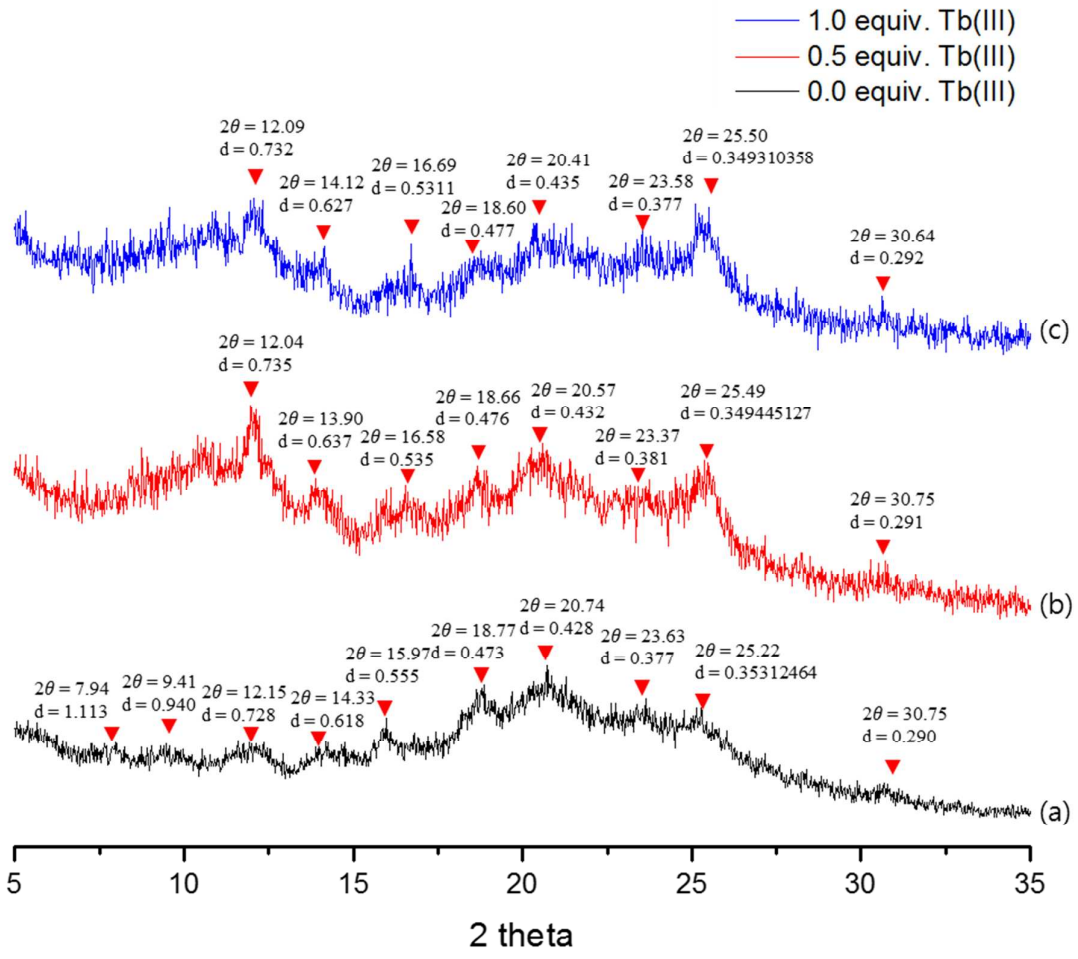

Figure S15. Powder XRD patterns of (a) gel-**1** (1.30×10^{-3} M), (b) gel- Tb(III) (0.5 equiv.), and (c) gel-Tb(III) (1.0 equiv.).

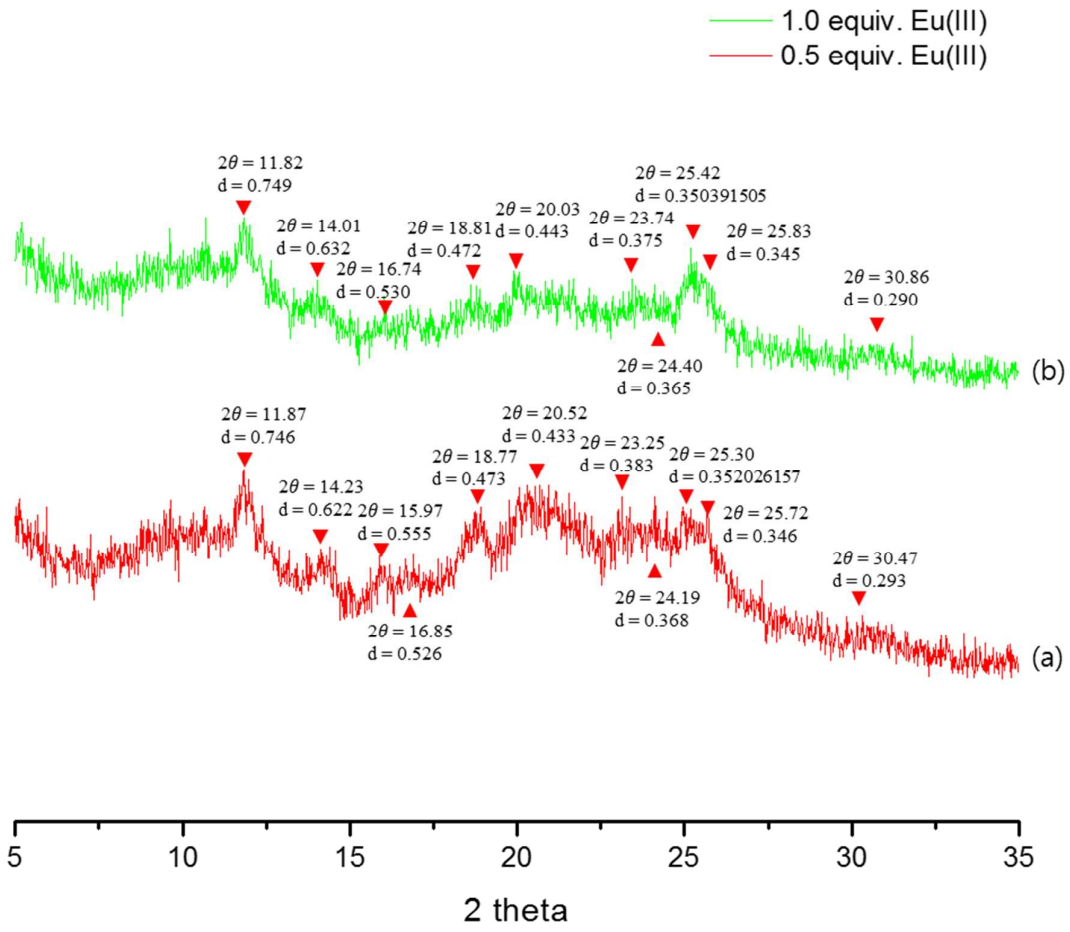

Figure S16. Powder XRD patterns of (a) gel-Eu(III)(0.5 equiv.), and (b) gel-Eu(III) (1.0 equiv.) (1.30×10^{-3} M).

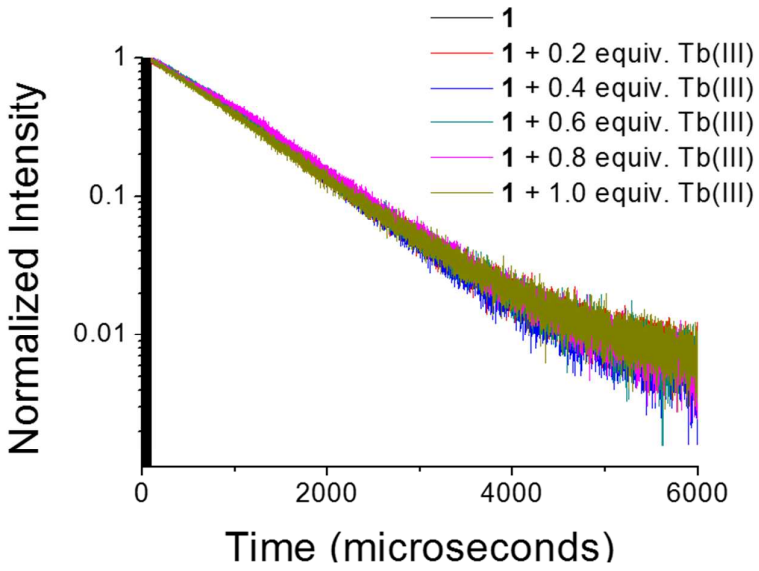

Figure S17. Emission decay curves of gel-**1** (1 wt%) and gel–Tb (0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 equiv.) in H_2O/DMSO (3:7v/v) (cell width : 2 mm).

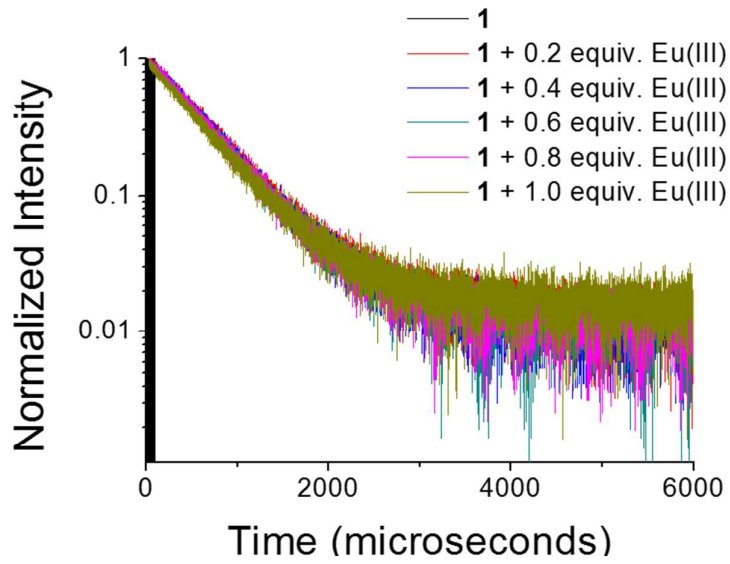

Figure S18. Emission decay curves of gel-**1** (1 wt%) and gel–Eu (0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 equiv.) in H_2O/DMSO (3:7v/v) (cell width : 2 mm).

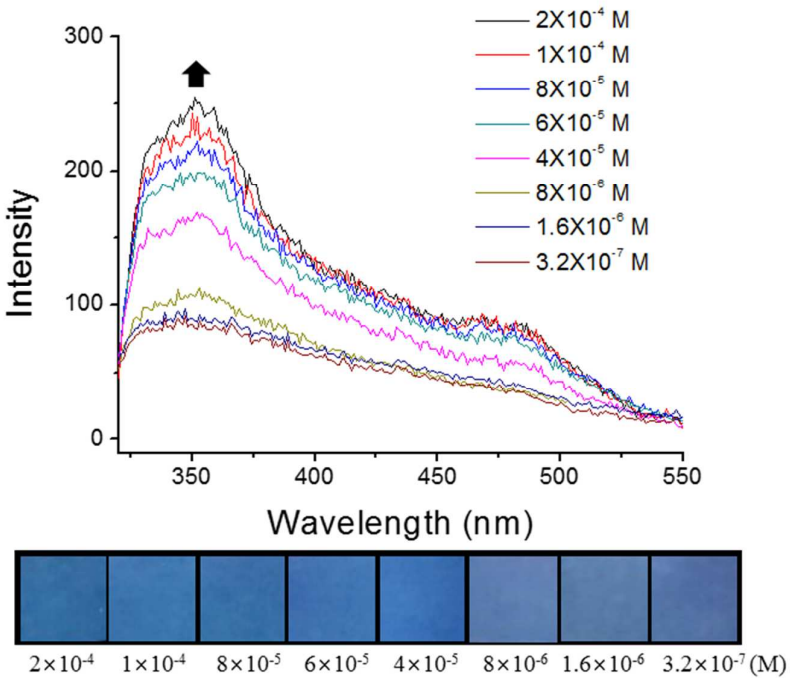

Figure S19. Luminescence spectra of gel-**1** coated papers (gel-**1**-P) at various concentrations.

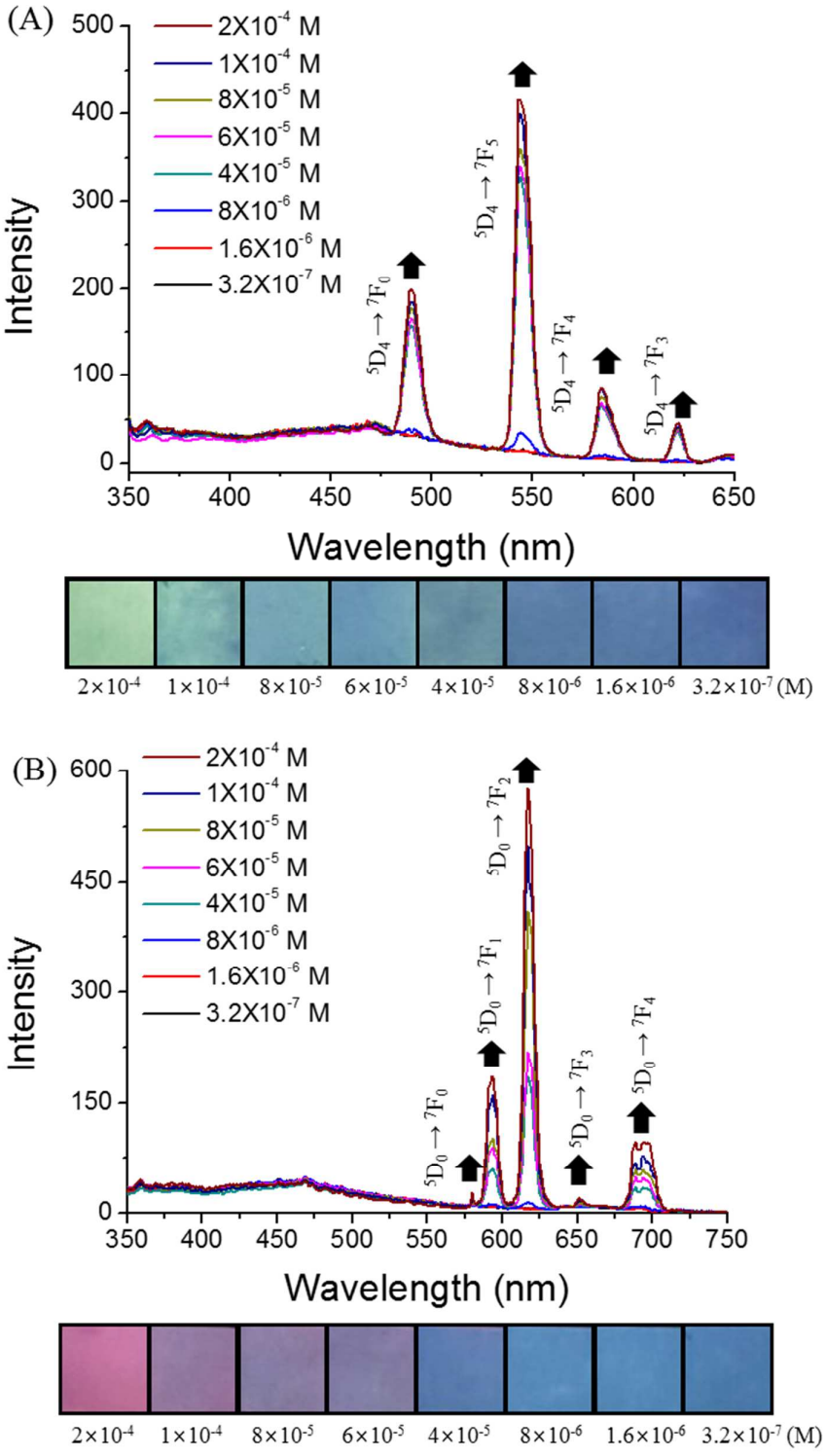

Figure S20. Luminescence spectra of various concentrations of (A) Tb(III) and (B) Eu(III) solution on the gel-**1**-P.

Table S1. Gelation test of **1** (1 wt%) with in the presence of Tb(III) (1 equiv.) and Eu(III) (1 equiv.) in various solvents.

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Solvent/DMSO mixture	Tb(III) state	Eu(III) state
Chloroform	S	S
Methylene chloride	S	S
Toluene	S	S
Methanol	S	S
Ethanol	S	S
Ethyl acetate	S	S
Acetonitrile	S	S
Tetrahydrofuran	S	S
Acetone	S	S
Water	G	G

S : Soluble, G : Gel

Table S2. Luminescence lifetimes of gel-**1** with different concentration of Tb(III) and Eu(III) (0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 equiv.).

Equivalent	Tb(III) (μs)	Eu(III) (μs)
0.0	0.0017	0.0017
0.2	925.1	536.9
0.4	926.7	549.5
0.6	946.1	560.0
0.8	947.8	565.8
1.0	1008	568.5

Instruments. A Bruker ARX 300 apparatus was used to observe the NMR spectra for ^{1}H and ^{13}C NMR. KBr pellets were prepared for the IR spectra and a Shimadzu FT-IR 8400S instrument was used to measure the IR spectra in a range of 400-4000 cm^{-1}. In addition, a JEOL JMS-700 mass spectrometer was used to measure the mass spectra. The absorption spectra in the gel and the solution were obtained using a UV-vis spectrophotometer (Thermo Evolution 600), and the fluorescence spectra were obtained using a RF-5301PC spectrophotometer, which was used for the variable-temperature emission measurements. These observations were conducted with a single-cell to control the working temperature in a range of 25 $^{\circ}C$–90 $^{\circ}C$. A 0.50 mm path length quartz cuvette and a 4 mm path length quartz cuvette were used to measure emissions from the gels.

Electron Microscopy. To examine the samples, a JEOL JEM-2010 transmission electron microscope operating at 200 kV was used at a 16 mm working distance with an accelerating voltage of 100 kV. An XE-100 and a PPP-NCHR 10 M cantilever (Park systems) were used to perform atomic force microscope (AFM) imaging. The AFM samples of gels were spin-coated (1500 rpm) onto newly cleaved Muscovite Mica, and images were taken at a moderate scan rate (0.3 Hz) with an AFM operating in the noncontact mode in air at RT with resolution of 1024 × 1024 pixels.

Rheological Measurements. A rheometer (AR-2000ex, TA Instruments Ltd, New Castle, DE, USA) was used to determine the mechanical properties of fresh terpyridine gels. Cone-type geometry of 40 mm diameter was used in the entire experiments. The dynamic oscillatory behavior was determined at a frequency of 0.1 rad s^{-1}. Furthermore, the response to oscillations of larger amplitudes was observed with up to 100% apparent shear strain and frequency sweeps in a range of 0.1 – 100 rad s^{-1} at 25 $^{\circ}C$.

Fluorescence Lifetime Measurements. The fluorescence lifetimes were determined using a conventional laser system through generation with an excitation source (420 nm output of a Spectra-Physics Quanta-Ray Q-switched GCR-150-10 pulsed Nd:YAG laser). A Hamamatsu R928 PMT was used to obtain fluorescence decay signals, which were recorded on a Tektronix model TDS-620A (500 MHz, 2 GS/s) digital oscilloscope and exponentially fitted for analysis.

Fluorescence Microscopy. Images were recorded using a Nikon Microscope ECLIPSE 80i with a 420 nm UV light excitation source. The emission spectra between 400 nm to 650 nm were observed with 100x magnification. The samples for microscopic images were prepared onto a glass slide by the drop-casting method and allowing for slow evaporation. Fluorescence quantum yields were determined by reference to rhodamine 6G ($\Phi = 0.88$)[1]

Typical Experimental Procedure for the Formation of Terpyridine-Based Supramolecular Gel. Compound **1** (4 mg, 1.0 wt%) was dissolved in DMSO (0.28 mL) and mixed with $Tb(NO_3)_3$ or $Eu(NO_3)_3$ (0-1.0 equivalent) dissolved in H_2O (0.12 mL). The mixture solution was kept at room temperature to form the gel.

Titrations and Binding Constants. UV−vis and luminescence titrations of a solution of **1** (5×10^{-4} M) with $Tb(NO_3)_3$ and $Eu(NO_3)_3$ (0 → 6 equiv.) at 298 K were used to confirm the formation of the luminescent (M:L, where M = Tb(III), Eu(III) and L = terpyridine-based ligand **1**) species. The nonlinear regression analysis program, SPECFIT was used to fit the data. For convergence of the data, each titration was repeated at least three times while evaluating the binding constant values.

Patterns of Supramolecular Gels by Inkjet Printing. Two ink solutions were prepared in deionized water (Ink A: Tb(III), 1 mM; Ink B: Eu(III), 1 mM). The inkjet printing was carried out at room temperature without any additional apparatus. An HP Deskjet Ink Advantage K209 a-z printer was used for printing on a modified A4-sized paper. Inkjet printing was conducted on the paper in the order of Ink A, and then Ink B. The emission colors of text and images on A4 paper by Microsoft program were assigned as a green ink for Tb(III) solution and a blue ink for Eu(III) solution.

Circular Dichroism Studies. A Jasco J-815 CD spectrophotometer with a quartz cell (0.1 mm path length) across the range of 200 to 500 nm was used to examine the circular dichroism (CD) spectra. The scanning was conducted at a rate of 50nm/min at sampling intervals of 1.0 nm and a response time of 1s to obtain the scans of the samples in DMSO and water at room temperature. The CD spectra of gel-**1**, gel-Tb and gel-Eu (1.30×10^{-3} M) at different metal concentrations (0, 0.25, 0.5, 1.0 equiv.) were also obtained. Circularly polarized luminescence and total luminescence spectra were obtained by previously reported method,[2] operating in a differential photon-counting mode. CPL measurements were performed at 295 K in DMSO and H_2O with analyte concentrations of 1.30×10^{-3} M.

REFERENCES

(1) Olmsted, J. Calorimetric Determinations of Absolute Fluorescence Quantum Yields. *J. Phys. Chem.* **1979**, *83*, 2581-2584.
(2) Riehl, J. P.; Muller, G. Handbook on the Physics and Chemistry of Rare Earths; *Circularly Polarized Luminescence Spectroscopy from Lanthanide Systems*. North-Holland Publishing Company, Amsterdam, Netherlands, 2004, 34, pp 289-357.